1.2 – Swimming Pool Water Buffer Chemistry

Buffering is the resistance of water to pH change. Water itself has little buffering in the 5 to 9 pH range. Therefore, buffering agents are necessary to prevent severe pH fluctuations that would otherwise occur when acidic or basic sanitizers are added to pool water. The presence of alkalinity in the form of bicarbonate and cyanurate imparts buffering to swimming pool water. A buffer system consists of a weak acid and its anion (e.g., carbonic acid and bicarbonate or cyanuric acid and cyanurate). A buffer system resists pH changes in either direction because it can react with either acidic or basic substances that are added to swimming pool water. However, because of the relatively low concentrations of buffering alkalinity (carbonate, cyanurate, or borate) in swimming pool water, the acid or base neutralizing capacity without significant pH change is limited. Although the buffers in swimming pools can neutralize minor quantities of acidic or basic substances with only small pH changes, significant pH changes will occur if large quantities of sanitizers (especially acidic) are added or if acid is added, eg, during pH adjustment. Maximum buffering occurs at a pH where the molar ratio of acid to anion is one. At 80°F and 1000 ppm TDS maximum buffering occurs at pH 6.3 and 6.8 for the carbonic acid/bicarbonate and cyanuric acid/cyanurate systems, respectively. By contrast, maximum buffering in the boric acid/borate system occurs at pH 9.2. On a molar basis, the cyanuric acid/cyanurate system provides more effective swimming pool water buffering at pH 7.5, 80°F, and 1000 ppm TDS because its pH of maximum buffering is closer to pool pH. However, on a ppm basis, the buffer intensity of the carbonic acid/bicarbonate and cyanuric acid/cyanurate systems are roughly comparable over the recommended pH range (7.2-7.8) and greater than that of borate at pH < 7.8. At pH 7.8, the buffering of the three systems are roughly comparable on a ppm basis. At and above pH 7.8, borate significantly supplements swimming pool buffering.

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Buffering

Buffering is the resistance of water to pH change. Water itself has virtually no buffering in the 5 to 9 pH range because of the low concentrations hydrogen (H^+) and hydroxyl ions (OH^-). Thus, buffers are necessary to prevent severe pH fluctuations when acidic or alkaline substances are added to pool water. For example, addition of only 3 ppm of gaseous chlorine to pure water at 25°C would decrease the pH from its normal value of 7.0 to 4.4 due to the hydrogen ions formed by hydrolysis of chlorine ($Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl$). By contrast, if 100 ppm of bicarbonate alkalinity was present in the water at the same pH, the pH would have decreased to only 6.95. This is due to the fact that bicarbonate reacts with hydrogen ions released by ionization of the hydrochloric acid (formed by hydrolysis of chlorine) minimizing the change in pH. A solution whose pH changes on addition of acid or base by much less than pure water is considered to be buffered.

Buffer Systems

A buffer system typically consists of two species, e.g., a weak acid and its anion (Wojtowicz 1995b). The acid is capable of reacting with basic hydroxyl ions and the anion with acidic hydrogen ions, e.g., carbonic acid and bicarbonate ion. The pH of a buffer depends on the ratio of acid to anion. This can be shown by mathematical analysis of the ionization of carbonic acid into hydrogen and bicarbonate ions.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

The ionization equilibrium constant (K_a) is given by:

Acid	Anion	pH of Maximum Buffering at 80°F and 1000 ppm TDS
carbonic, H_2CO_3	bicarbonate, HCO_3^-	6.3
cyanuric, $H_3(NCO)_3$	cyanurate, $H_2(NCO)_3^-$	6.8
boric, $B(OH)_3$	orthoborate, $B(OH)_4^-$	9.2

Table 1 – Buffer Systems Important in Swimming Pools

$$K_a = [H^+][HCO_3^-] / H_2CO_3$$

The following equation for the pH of a buffer is obtained by taking logs and rearranging.

$$pH = pK_a + \log [HCO_3^-] / [H_2CO_3]$$

Maximum buffering occurs at a pH where the molar ratio of acid to anion is one. This pH is also equal to the pK_a of the acid which is the negative logarithm of the ionization constant. Below this pH, the base neutralizing capacity exceeds the acid neutralizing capacity, whereas, above this pH, the reverse is true. The practical pH range of a buffer is one pH unit above or below the optimum pH. Examples of buffer systems important in swimming pools are shown in Table 1. Table 1 shows that cyanuric acid is the better buffer because its pH of maximum buffering is closer to the swimming pool pH range.

Since bicarbonate ion has a replaceable hydrogen, it forms a second buffer system in combination with carbonate ion, which exhibits maximum buffering at pH 10.1. By contrast with carbonic acid, cyanuric and boric acids have three ionizable hydrogens and thus can potentially form three buffer systems (see previously published ionization diagrams for carbonic and cyanuric acids, Wojtowicz 1995a). However, only the first ionizations are of practical importance in pools.

The pH of human blood is maintained at 7.4 by a mixture of bicarbonate and phosphate buffers. At first glance the phosphate system, consisting of monophosphate ($H_2PO_4^-$) and diphosphate (HPO_4^{2-}) ions, appears potentially attractive for pools because it exhibits maximum buffering at pH 7.2. However, closer examination reveals that phosphate promotes the growth of algae and can also cause cloudy water because of precipitation of calcium phosphate which can occur at relatively low phosphate concentrations (~5 ppm). Therefore, phosphates are not recommended for swimming pool use.

Hypochlorous acid and hypochlorite ion also form a buffer system, with maximum buffering at pH 7.5. However, the concentration is too low to exert significant buffering. Mixtures of bases and their salts can also serve as buffers, e.g., ammonia and ammonium ion. However, this would not be practical for use in pools.

Strength of Buffering (Buffer Intensity)

The strength of buffering is measured by the buffer intensity (β) which is the incremental change in alkalinity required to change pH by one unit, i.e., β = ΔAlk/ΔpH. For a diprotic acid such as carbonic acid and its salts it is expressed numerically by:

$$\beta = 2.3\{C_T[\alpha_1(\alpha_0 + \alpha_2) + 4\alpha_0\alpha_2] + OH^- + H^+\} \cdot 50 \cdot 10^3 \text{ ppm } CaCO_3$$

Buffer	Concentration, M	Buffer Intensity (ppm $CaCO_3$)	
		Maximum*	at pH 7.5
cyanurate	0.002	57.5	30.4
bicarbonate	0.002	57.6	12.9
borate	0.002	59.3	4.6

*At pH of maximum buffering shown in Table 1.

Table 2 – Buffer Intensity of Swimming Pool Buffers

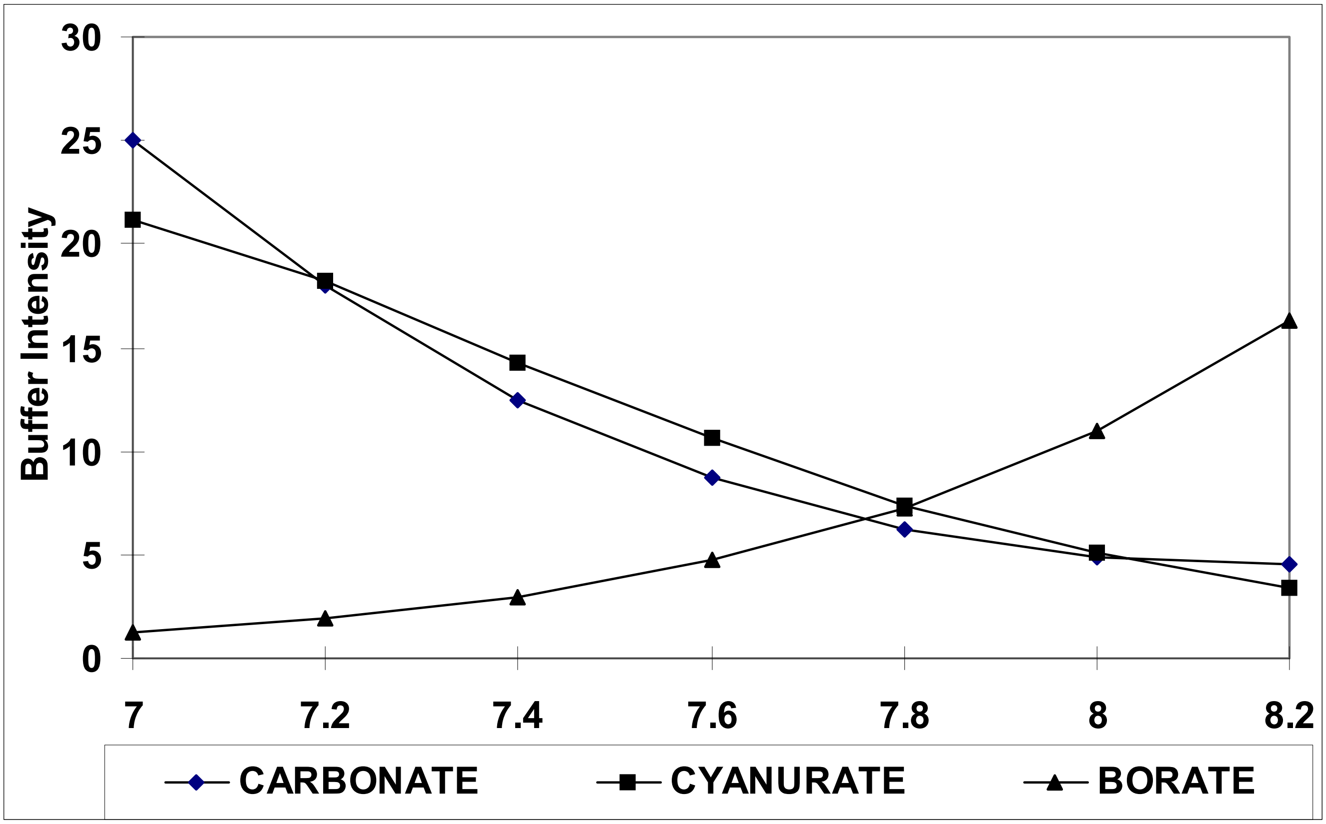

Figure 1 – Variation of Buffer Intensity with pH

where: C_T is the total molar concentration of carbonic acid, bicarbonate, and carbonate and α_0, α_1, and α_2 are the respective ionization fractions. Although buffer intensity is usually expressed as equivilents per liter, it is expressed here and elsewhere as ppm $CaCO_3$, similar to alkalinity. For a monoprotic acid and its salt it is given by the following equation:

$$\beta = 2.3(C_T\alpha_0\alpha_1 + OH^- + H^+) \cdot 50 \cdot 10^3 \text{ ppm } CaCO_3$$

Although cyanuric acid is a triprotic acid (i.e., it has three ionizable hydrogen atoms), the ionization of only the first hydrogen is important at pool pH. Thus, the above equation can be used to calculate its buffering effect; where: C_T is the sum of the concentrations of cyanuric acid and cyanurate ion and α_0 and α_1 are the respective ionization fractions. This equation can also be used for boric acid. In the pH range important to swimming pools, the contribution of hydrogen and hydroxyl ions to the buffer intensity can be neglected because of the low concentration of these ions. For example, the buffer intensity of water itself at pH 7.5 is equivalent to only 0.04 ppm $CaCO_3$.

Buffers for laboratory use typically have concentrations in the 0.02–0.05 molar range. By contrast, the concentration of buffering agents in swimming pools is much lower, consequently the buffering effect is correspondingly less; e.g., 100 ppm of bicarbonate alkalinity is equivalent to only 0.002 molar. Calculated buffer intensities for 0.002 M bicarbonate, borate, and cyanurate buffers at pH 7.5, 80°F, and 1000 ppm TDS are tabulated in Table 2.

Because the pH of maximum buffering of the typical buffering agents found in swimming pools lies outside the normal pH range of pools, the buffering strength is less than optimum. On a molar basis, cyanurate has the higher buffer intensity of the three buffers listed at pool pH.

Variation of Buffer Intensity with pH

Buffer intensity increases not only with the concentration of carbonate, cyanurate, and borate alkalinity but it also varies with pH because the ratio of acid to anion changes with pH. This is shown graphically in Figure 1 where buffer intensity is plotted as a function of pH. By contrast to water, the buffer intensity of weak acid–derived alkalinity (i.e., carbonate, cyanurate, and borate) is significant in the 5–9 pH range. The graph shows that the

pH	Carbonate	Cyanurate	Borate
7.0	25.0	21.2	1.2
7.2	18.0	18.2	1.9
7.4	12.5	14.3	3.0
7.6	8.7	10.6	4.7
7.8	6.2	7.4	7.3
8.0	4.9	5.1	11.0
8.2	4.5	3.4	16.3

Table 3 – Variation of Buffer Intensity with pH
80°F, 1000 ppm TDS, acid + anion concentration 100 ppm

buffer intensity of carbonate and cyanurate alkalinity decrease with increasing pool pH. By contrast, the buffering intensity of borate alkalinity increases with increasing pool pH. Both carbonate and cyanurate systems provide roughly comparable buffering over the entire pool pH range (see Table 3). Compared to either carbonate or cyanurate alkalinity, the buffering effect of borate is significantly less below pH 7.8, but greater above pH 7.8. Thus, borate significantly supplements the buffering of pool water at pH ≥ 7.8.

Buffer Chemistry

Acid or Base Neutralizing Capacity of Buffers – Because of the relatively low concentrations of buffering alkalinity in swimming pool water, the acid or base neutralizing capacity without significant pH change is limited. The carbonic acid/bicarbonate system has a greater capacity for neutralizing acid than base because the ratio of bicarbonate ion to carbonic acid is about 17 at pH 7.5, 80°F, and 1000 ppm TDS. Although the buffers in swimming pools can neutralize minor quantities of acidic or basic substances with only small pH changes, significant pH changes will occur if large quantities of sanitizers (especially acidic) are added or if sufficient acid is added, e.g., during pH adjustment.

Effect of Basic Species – The carbonic acid/bicarbonate system is one of the simplest buffers. If a strong base (e.g., NaOH present in small amounts

Hypochlorite	Treatment	oz/week	ΔpH/week
Sodium	maintenance	56.0	+1.5
Sodium	shock	106.5	+1.7
Calcium	maintenance	10.5	+1.2
Calcium	shock	20.0	+1.4

Table 4 – pH Changes due to Alkaline Sanitizers in Unbuffered Water
pH 7.0, 80°F

Hypochlorite	Treatment	oz/week	ΔpH/week
Sodium	maintenance	56.0	+0.02
Sodium	shock	106.5	+0.04
Calcium	maintenance	10.5	+0.01
Calcium	shock	20.0	+0.02

Table 5 – pH Changes due to Alkaline Sanitizers in Typical Pool Water
pH 7.5, 80°F, Carb. Alk. 100 ppm, Cyanuric Acid 100 ppm, TDS 1000 ppm

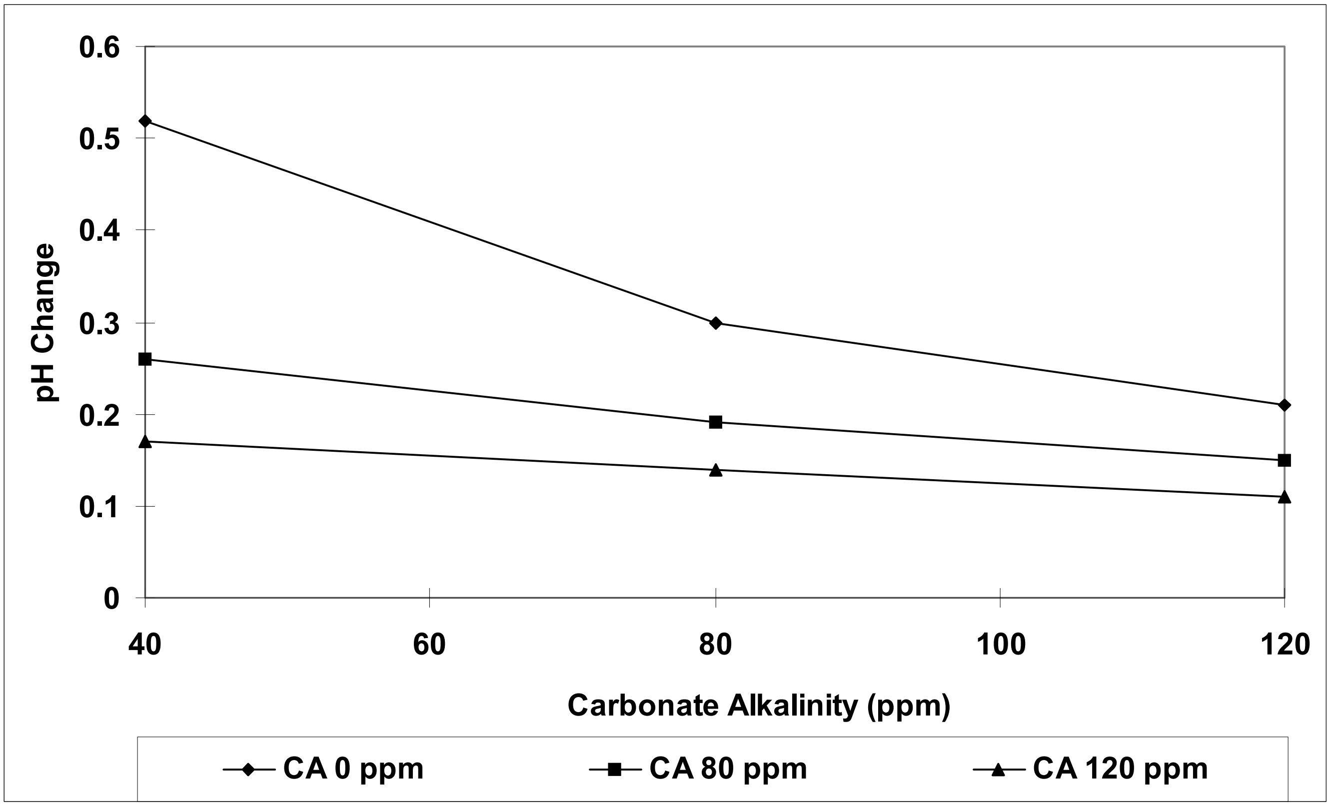

Figure 2 – pH Change Due To Hypochlorite Ion During Shock Treatment

in liquid bleach or $Ca(OH)_2$ present in small amounts in calcium hypochlorite) is added to water containing carbonic acid and bicarbonate ion, the OH^- ions (formed by ionization of NaOH or $Ca(OH)_2$) will be neutralized by carbonic acid according to the following reaction:

$$OH^- + H_2CO_3 \rightleftharpoons H_2O + HCO_3^-$$

Since the equilibrium for this reaction lies far to the right, the added hydroxyl ions are completely removed. There is a small decrease in the carbonic acid concentration and a small increase in the bicarbonate ion concentration, consequently there is a small increase in pH. Cyanuric acid functions similar to carbonic acid:

$$OH^- + H_3(NCO)_3 \rightleftharpoons H_2O + H_2(NCO)_3^-$$

Table 4 shows pH changes due to maintenance and shock treatment doses of calcium and sodium hypochlorite in unbuffered water at an initial pH of 7.0 and 80°F. The calculated data show very large pH changes in the absence of buffering.

Table 5 shows calculated pH changes in buffered pool water due to maintenance and shock treatment doses of calcium and sodium hypochlorite at an initial pH of 7.5, 80°F, 100 ppm carbonate alkalinity, 100 ppm total cyanurate, and 1000 ppm TDS. The pH changes are only a fraction (i.e., 1–2%) of those in unbuffered water.

Effect of Alkaline Species – Although the low concentration of strong base present in hypochlorite sanitizers has a small effect on swimming pool pH, the hypochlorite ion provided by these sanitizers exerts a much greater effect on pH because of its higher concentration. Hypochlorite ion will increase pH by consuming hydrogen ions as shown below.

$$ClO^- + H^+ \rightleftharpoons HOCl$$

At normal av. Cl levels this has a small effect on pH, e.g., $\Delta pH = 0.04$ at $pH_i = 7.5$, 80°F, av. Cl dose 3 ppm, 100 ppm carbonate alkalinity, 100 ppm cyanuric acid, and 1000 ppm TDS. However, at shock treatment doses (i.e., 10 ppm av. Cl), the pH

	ΔpH*		
Carb. Alk., ppm	**CA = 0 ppm**	**CA = 50 ppm**	**CA =100 ppm**
40	0.52	0.26	0.17
80	0.30	0.19	0.14
120	0.21	0.15	0.11

*Includes small contribution from $Ca(OH)_2$ and $CaCO_3$.

Table 6 – pH Changes During Shock Treatment With $Ca(ClO)_2$
pH_i 7.5, 80°F, Av. Cl dose 10 ppm, 1000 ppm TDS

change would be significantly higher (i.e., ΔpH = 0.12) under similar conditions. However, this would only be a temporary pH change because decomposition would convert all of the original hypochlorite ion to chloride ion which has no effect on pH. Table 6 shows calculated pH changes due to a shock treatment dose of hypochlorite under different conditions of buffering. The data are also shown graphically in Figure 2.

When sodium tetraborate (i.e., borax $Na_2B_4O_7$) is added to water it ionizes to sodium and tetraborate ions:

$$Na_2B_4O_7 \rightarrow 2Na^+ + B_4O_7^{2-}$$

The tetraborate ion is a polynuclear complex that hydrolyzes to an equilibrium mixture of boric acid and orthoborate ion.

$$B_4O_7^{2-} + 7H_2O \rightleftharpoons 2B(OH)_3 + 2B(OH)_4^-$$

At low concentrations (≤ 0.025 M, ≤ 5035 ppm $Na_2B_4O_7$), the equilibrium lies completely to the right (Cotton 1988). Thus, tetraborate will raise pool pH because one of its hydrolysis products neutralizes hydrogen ions via the following reaction:

$$B(OH)_4^- + H^+ \rightleftharpoons B(OH)_3 + H_2O$$

The equilibrium for this reaction lies far to the right at pool pH. The pH change will depend on the concentration of tetraborate added. Addition of large quantities can have a large effect on pH. For example, addition of 100 ppm of $Na_2B_4O_7 \cdot 5H_2O$ to pool

Carbonate Alkalinity, ppm	Total Cyanurate, ppm	ΔpH/week
0	0	–3.7
50	0	–0.55
50	50	–0.38
100	0	–0.33
100	100	–0.22

Table 7 – Calculated pH Changes for Maintenance Doses of Chlorine
pH 7.5, 80°F, Cl_2 6.8 oz/week, TDS 1000 ppm

Sanitizer	oz/week	ΔpH/week
chlorine gas	6.8	–0.22
Trichlor	7	–0.14
Dichlor	10.5	–0.09

Table 8 – Calculated pH Changes Due to Acidic Sanitizers
pH 7.5, 80°F, Carb. Alk. 100 ppm, Cyanuric Acid 100 ppm, TDS 1000 ppm

Carbonate Alkalinity, ppm	Cyanuric Acid, ppm	ΔpH/week
40	0	+0.17
40	50	+0.07
40	100	+0.05
80	0	+0.44
80	50	+0.24
80	100	+0.16
120	0	+0.68
120	50	+0.41
120	100	+0.30

Table 9 – pH Changes due to Loss of Carbon Dioxide
pH_i 7.5, 80°F, 1000 ppm TDS

water at pH 7.5 and 80°F with 100 ppm carbonate alkalinity, 100 ppm cyanuric acid, and 1000 ppm TDS would raise the pH to 8.7.

Effect of Acidic Species – When chlorine is added to pool water, it hydrolyzes to a mixture of hydrochloric and hypochlorous acids. Decomposition of hypochlorous acid produces more hydrochloric acid. Thus, all of the added chlorine is eventually converted to hydrochloric acid. Ionization of hydrochloric acid produces hydrogen ions which react with bicarbonate ion to form carbonic acid as shown below.

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3$$

The equilibrium for this reaction lies far to the right. Thus, all of the hydrogen ions introduced by the hydrochloric acid are neutralized. A decrease in

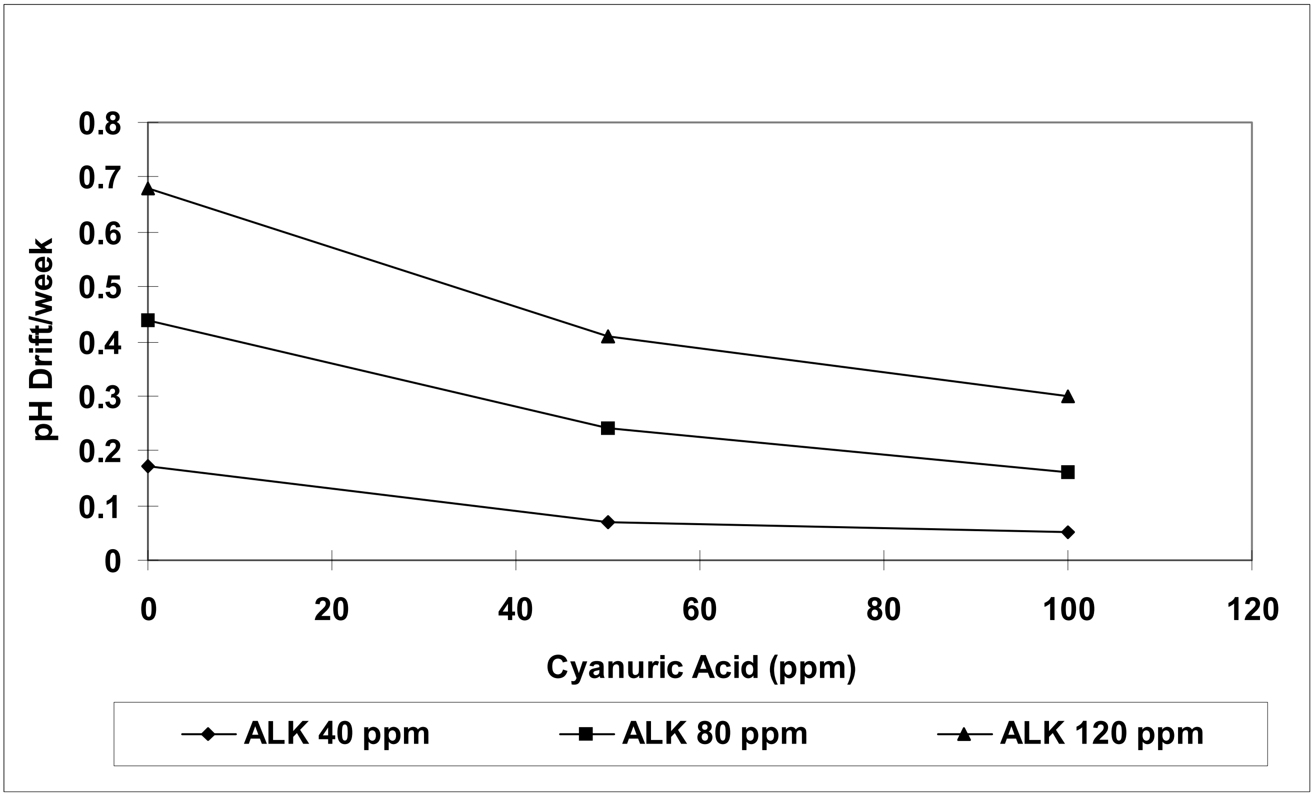

Figure 3 – Effect of Alkalinity and CA on pH Drift Due to CO_2 Loss

pH and alkalinity will occur, the extent depending on how much HCl is formed, a shock treatment dose causing a larger change than a maintenance dose.

Other acid forming sanitizers are Dichlor and Trichlor. On complete decomposition they form a mixture of hydrochloric and cyanuric acids (Wojtowicz 1995b). Since cyanuric acid does not ionize completely as does hydrochloric acid, it has somewhat less effect on pH. Table 7 shows the weekly change in pH for maintenance doses of chlorine (6.8 oz/week) with and without buffering at 80°F, initial pH 7.5, and 1000 ppm TDS. The calculated data show that the pH change decreases with increasing concentration of carbonate and cyanurate alkalinity.

Table 8 shows the weekly change in pH caused by acidic sanitizers. The calculated data show that on a daily basis, that the pH changes are quite small due to the buffering action of pool water. However, a single shock treatment dose (13 oz) of chlorine would result in a pH change of –0.37, a greater change than a weeks worth of maintenance doses.

Effect of Carbon Dioxide Loss – Another factor that affects pH is loss of carbon dioxide (Wojtowicz 1995c). Loss of carbon dioxide raises pH because it decreases the ratio of carbonic acid to bicarbonate ion. The calculated pH drift, based on test data for an outdoor pool without bathers for a 20,000–gal pool (6 feet average depth) at pH 7.5, 80°F, and 1000 ppm TDS, and a turnover rate of 0.84 (8–hr pump duty cycle and 35 gal/min pumping rate) are given in Table 9. The pH in all of these examples will tend to level off at pH 8.3. The calculated data illustrate the buffering effect of cyanuric acid with a decreasing pH rise with increasing cyanuric acid concentration at constant carbonate alkalinity (see Figure 3). By contrast, the pH rise increases with increasing carbonate alkalinity at constant cyanuric acid concentration. This is due to the fact that the CO_2 loss rate varies with the square of the carbonate alkalinity, whereas, buffering varies with the first power of carbonate alkalinity.

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